Enhancement in mineralization of a number of natural refractory organic compounds by the combined process of sonolysis and ozonolysis (US/O_3)

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Introduction

The presence of refractory organic macromolecules such as humic acid (HA) and tannic acid (TA) in piggery wastewater; leachate, tannery, dye, or olive mill wastewater (OMW); pulp/paper wastewaters, etc. [1,2] makes it difficult to effectively treat such wastewaters through biological treatment processes [3].

Tannins are water-soluble polyphenol compounds that are widely prevalent in plants and plant residues [4]. Tannins have large molecular weights ranging from 500 to 4000 Da and a strong affinity to proteins, alkaloids and heavy metals to form complex molecules [5]. Hydrolysable and condensed tannins are the two major classes of tannins [4]. These compounds have a range of effects on various organisms, from toxic effects on animals to growth inhibition of microorganisms [6]. Hydrolysable tannins are principally multiple esters of D-glucose with gallic acid and its oxidative metabolites, while condensed tannins (proantocyanidins) are comprised of flavan-3-ol units linked through a CAC bond [5]. Humic substances are created by the microbial degradation of plant and animal tissues and ultimately by the dispersal of biomolecules (lipids, proteins, carbohydrates, and lignin) in the environment after the death of living cells. HA has large molecular weights ranging from 4000 to 300,000 Da [7,8].

The ultrasonic irradiation for aqueous solutions has been shown to be effective in the in situ destruction of a variety of organic and inorganic contaminants [9]. The ultrasonication causes a cavitation effect, which results in a high temperature (5000 K) and pressure (1000 atm). The main reaction mechanisms are _OH radical reaction, pyrolysis and micro-jets. The combined operation of sonolysis (US) and O_3 renders a synergistic effect in the destruction of organic matter [10,11]. The synergy is due partly to an excess of hydroxyl radicals formed upon the thermal decomposition of O_3 in the gas phase and partly to an increased mass transfer of ozone in solution by the mechanical effects of US. A simplified reaction scheme for the generation of the _OH radical during the US/O_3 treatment of

water is as follows [10]:

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These decomposition reactions occur in the gas phase. The products of the reaction migrate to the interface of the bubble where they subsequently react. The mechanism of the US and O_3 combined process is as follows:

1. When water is ozonated during ultrasonic irradiation, the synergistic increase in the production of hydroxyl radicals is due to an additional pathway that involves the thermal decomposition of ozone [10,12].

2. A further advantage of such a combination is the enhanced O_3 transfer in solution, resulting from larger gas diffusion coefficients in the presence of ultrasonic vibrations than in non-irradiated solutions [12].

Naddeo et al. [13] reported the removal of organic matter during ultrasonic irradiation, and Saroj et al. [14] reported the mineralization of some natural refractory organic compounds by ozonation and mineralization of phenol in aqueous solution by ozonation using iron or copper salts and light [15]. Killops [16] and Gilbert et al. [17] reported that ozonation led to a rapid decolorization and to a decrease in the UV-absorbance of humic substances due to a loss of aromaticity. This is attributed to the de-polymerization of the humic materials [18]. Because phenolic and acidic compounds were detected as by-products of humic substances, the TOC was either reduced [18] or unchanged. The ozonation of humic substances also led to the formation of small molecules, mainly aldehydes and carboxylic acids, which accumulate in the solution due to their resistance towards further degradation by ozonation [19–21].

The use of O_3 in advanced oxidation processes (AOPs) is widely popular, with the advantage that O_3 reacts with organic compounds either directly in acidic/neutral conditions and/or indirectly by decomposition in a highly alkaline pH [22]. The rate-limiting parameter in the decolonization of azo dye solutions by O_3 is the mass transfer rate of ozone in the solution [23]. O_3 is able to oxidize a large amount of organic matter. Also, because SH@S, ANH_2, @NH, AOH are combined with CHO, there is a possibility of an easy reaction. Ince and Tezcanli [24] reported the removal of reactive dyestuff in wastewater by an US/O_3 combination. Weavers et al. [9] studied the kinetics and mechanism for the removal of pentachlorophenol (PCP) by use of US/O_3, the removal of methyl tert-butyl ether by the combined US/O_3/H_2O_2 combined process [25], and

aromatic compound degradation in water using a combination of US and O_3 (US/O_3) [12]. Tezcanli-Guyer and Ince [26] reported the removal of textile dyes by a US/O_3/UV combination, and the degradation of aniline in aqueous solution by the US/O_3 combination [27]. Son et al. [28] studied the use of the US/O_3 combination for the removal of aqueous tannin.

The objective of this study was to investigate and compare the effects of sole US or O_3 and the combination of US and O_3 for the synergetic oxidation in AOPs. This research also included the exploration for the extent of mineralization, the reduction in color, and the reduction of COD_{Cr} and TOC of HA and TA by the sole US or O_3 and US/O_3 combined treatments.

Material and methods

Experimental tests for the following three models of US, O_3, and US/O_3 were carried out with a pure solution of the model compounds.

2.1. Model compounds

The two model compounds used were tannin, AR Grade (Gallotannic acid; Molecular formula: $C_{76}H_{52}O_{46}$; Molecular weight: 1701.23: Minimum assay: 90%; Supplier: Fine-Chem. Ltd., Mumbai, India), humic acid, and LR Grade (CAS No 68131-04-4, Molecular weight: 5505, ALDRICH Chemicals, US). The carbon, hydrogen, nitrogen and oxygen content of these compounds were estimated using an elemental analyzer (Model EA1110, CE Instrument, Italy), and the results obtained are presented in Table 1 Since the analytical results for the effluent of biological treatment for livestock wastewater were 64 and 182 mg L_{-1}, similar concentrations of HA and TA were prepared using the standard chemicals of HA and TA. Experiments were conducted at the frequencies of 35 kHz for US and with 71 g m^{-3} (2 LPM) of O_3 concentration.

2.2. Experimental protocol

Experiments were carried out in three phases. Experiments in phase 1 consisted of ultrasonic irradiation for each model compound. The phase 2 experiments included the ozonation of aliquots of pure model compounds while the experiments of phase 3 incorporated the combined process of US/O_3 for the aliquots of pure model compounds, HA and TA. The parameters monitored in all phases were pH, color, TOC, COD, organic compounds detected

by GC/MS, and molecular distribution analyzed by the ultra filtration method.

2.3. Setup for the ultrasonication

The system, illustrated schematically in Fig. 1, consisted of a 2 L stainless-steel pentagon reactor, a generator with a maximum power of 500 W, piezoelectric transducers (emitting at 35, 72, 100, and 170 kHz) mounted on three lateral walls, and three quartz windows.

2.4. Setup for ozonation

The experimental setup used for ozonation consisted of a bubble contactor operated in the semi-batch mode shown in Fig. 1. O_3 was generated in a gas phase by passing the pure dry oxygen through the O_3 generator (LAB 2B model). Arrangements were made for applying this gas mixture to the bottom of the reactor, where it bubbled through a porous ceramic plate and moved upwards through the reactor. The O_3 concentration in the gas influent to and effluent from the reactor was measured using an online O_3 monitor (O_3 Instrumentation; Model: H1-S; USA). All components of the experimental setup and the reactor were fabricated of glass, Teflon or stainless steel in order to ensure the complete elimination of O_3 consumption caused by the corrosion of components due to ozone, which leads to erroneous experimental results.

2.5. Analytical methods

The pH of the solution was measured using a pH electrode (Thermo Orion model 420A_+) connected to a digital pH meter. The COD_{Cr} of the samples was analyzed by use of the closed reflux method as described in Standard Methods (Method No. 5220C, APHA, 1995). The color of the samples was analyzed by the visual examination as described in Standard Methods (Method No. 2120 B, APHA, 1995). For the TOC determination, samples were analyzed using a TOC analyzer (Model Sievers 5310C TOC analyzer and a Sievers 900 auto sampler GE Jena USA). The absorbed ozone concentration was analyzed using the ozone analyzer meter (Model H1 analyze, USA). GC/MS was used to analyze the by-products [GC: GC condition Agilent 6890 gas chromatograph and a Column DB-XLB (25 m anallmy-prodlm), MS: MS condition TOF-MS Pegasus III, Leco corporation, Ionization mode Electron impact (EI) and EM voltage 1500 volts (Injection volume 1 lL)].

To confirm the generation of the carbonyl compounds among the final products for the US/O_3 combined treatment, the sample was selected after 2 h of reaction, was pre-treated with Pentafluorobenzyl

hydroxylamine, and was analyzed by the PFBOA method of GC/MS. For the emulsification of the sample, 0.6 mL of PFBOAHCl and 1 mL of 0.1 M thiosulfuric sodium were placed into the 10 mL sample and were kept for 2 h at room temperature. Then, 0.16 mL of 18 N sulphuric acid and 4 g of salting out agent NaCl were mixed with the above emulsified sample. Finally, 1 mg L_{-1} decafluorobiphenyl included in 2 mL nucleic acid was placed into the prepared sample and shaken for about 1 h to extract the nucleic acid layer. The sodium sulfate was then placed into an extracted nucleic acid layer for dehydration. The derivative was analyzed by GC/MC, which has an EC-1 capillary column.

The molecular size distributions of the by-products were investigated using the ultra filtration method. The experimental condition of the ultra filtration method was shown in Table 2

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